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PAPER

## Anion-dependent construction of two hexanuclear 3d–4f complexes with a flexible Schiff base ligand†‡

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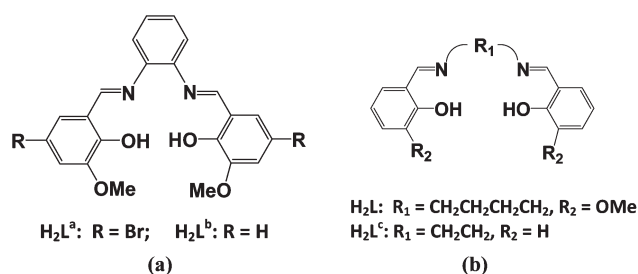
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Two hexanuclear 3d–4f Ni–Eu and Cu–Eu complexes  $[\text{Eu}_4\text{Ni}_2\text{L}_2(\text{OAc})_{12}(\text{EtOH})_2]$  (**1**) and  $[\text{Eu}_4\text{Cu}_2\text{L}_2(\text{OAc})_{12}] \cdot 2\text{H}_2\text{O}$  (**2**) are reported which are formed from the salen type Schiff-base ligand  $\text{H}_2\text{L}$  ( $\text{H}_2\text{L} = N,N'$ -bis(3-methoxysalicylidene)butane-1,4-diamine). In both complexes, four  $\text{Eu}^{3+}$  cations are bridged by eight  $\text{OAc}^-$  groups and the chain is terminated at each end by two ML ( $\text{M} = \text{Ni}$  and  $\text{Cu}$ ) units. The structures of **1** and **2** were determined by single crystal X-ray crystallographic studies and the luminescence properties of the free ligand and metal complexes in solution were measured.

## Introduction

The design and construction of polynuclear metal complexes have received extensive attention due to the fascinating physical and chemical properties associated with this class of materials.<sup>1</sup> Heteropolynuclear complexes comprised of d-block transition metals and lanthanide ions are currently of interest for potential applications in materials which harness unique optical and magnetic properties.<sup>2</sup> However, it is difficult to control the structures of polynuclear assemblies based on lanthanide ions because they often display high and variable coordination numbers and have no strong stereochemical preferences. Complex structures are often influenced by a variety of factors such as ligand architecture, the nature of counter ions, and ionic radii.<sup>3</sup> The majority of d–f polynuclear compounds reported so far have employed carboxylates, amino acids, betaines, and 2-pyridonates as ligands.<sup>4</sup> Compartmental Schiff bases with two dissimilar metal-binding sites, one being specific for the d metal ion and another for the f metal ion, are classical ligands which have been used for the synthesis of 3d–4f heteronuclear complexes.<sup>5a–d</sup> Our recent studies have focused on the synthesis of polynuclear 4f homometallic and 3d–4f heterometallic complexes with Schiff-base



Scheme 1 Salen-type Schiff base ligands.

ligands.<sup>5e–i</sup> We have employed essentially two kinds of “salen” style Schiff-base ligands in which one is a conjugated ligand with a phenylene backbone  $\text{H}_2\text{L}^{a,b}$  (Scheme 1a) and the other is exemplified by the flexible Schiff-base ligands  $\text{H}_2\text{L}^c$  and  $\text{H}_2\text{L}^d$  (Scheme 1b). In past studies, we discovered that “multi-decker” 4f and 3d–4f complexes with lanthanide ions sandwiched between alternating layers of the Schiff-base ligand  $\text{L}^a$  or  $\text{ZnL}^b$  units could be isolated.<sup>5e–g</sup> A key feature in these kinds of structures is the presence of intramolecular  $\pi$ – $\pi$  stacking interactions between planar conjugated Schiff base ligands, which can further add to the stability of the complex. When the more flexible Schiff base ligands  $\text{H}_2\text{L}^c$  and  $\text{H}_2\text{L}^d$  were used in the synthesis, a variety of 1-D coordination polymers were formed by bridging  $\text{H}_2\text{L}^c$  units or by  $\text{OAc}^-$  (acetate) anions.<sup>5h,i</sup> The flexible Schiff-base ligands show a “stretched” configuration to bridge lanthanide ions, forming coordination polymeric structures in which  $\pi$ – $\pi$  stacking interactions do not occur. We are interested in the influence of anions on the structures of these lanthanide complexes. For example, a 1-D coordination polymer  $\{\text{YbNiLCl}(\text{OAc})_2(\text{H}_2\text{O})\}_n$  was obtained from the reaction of  $N,N'$ -bis(3-methoxysalicylidene)butane-1,4-diamine ( $\text{H}_2\text{L}$ ) with  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  and  $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$  when there were two kinds of anions present in the reaction mixture,  $\text{OAc}^-$  and  $\text{Cl}^-$ . In contrast, a heterobinuclear complex  $[\text{YbNiLCl}_3(\text{H}_2\text{O})_3]$  was formed from

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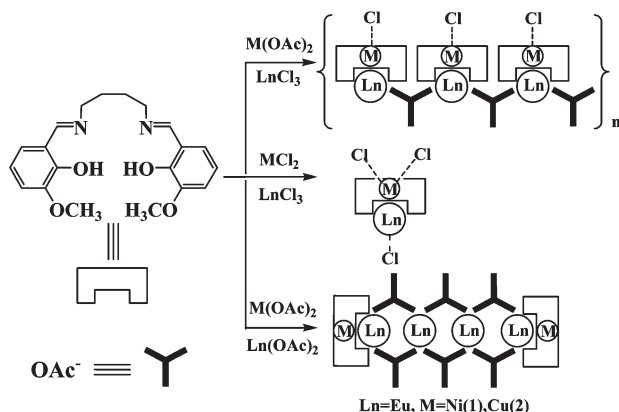
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†Dedicated to Professor David Cole-Hamilton on the occasion of his retirement and for his outstanding contributions to transition metal catalysis and Inorganic Chemistry.

‡Electronic supplementary information (ESI) available: NMR spectra of **1** and **2** (2 pages). CCDC 869086 and 869087. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt31268a



**Scheme 2** Synthesis of 3d–4f complexes **1** and **2**.

the reaction of  $\text{H}_2\text{L}$  with  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$  when the only anion that was present was  $\text{Cl}^-$  (Scheme 2).<sup>5i</sup> As part of our continuing studies focused on the construction of high nuclearity frameworks, we describe here two 3d–4f hexanuclear complexes  $[\text{Eu}_4\text{Ni}_2\text{L}_2(\text{OAc})_{12}(\text{EtOH})_2]$  (**1**) and  $[\text{Eu}_4\text{Cu}_2\text{L}_2(\text{OAc})_{12}] \cdot 2\text{H}_2\text{O}$  (**2**) which are obtained from reactions of  $\text{H}_2\text{L}$  with  $\text{M}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  ( $\text{M} = \text{Ni}(\text{II})$  and  $\text{Cu}(\text{II})$ ) and  $\text{Eu}(\text{OAc})_3 \cdot 4\text{H}_2\text{O}$  (Scheme 2). In these examples only  $\text{OAc}^-$  was present in the reaction mixture. Of the known heterometallic 3d–4f Schiff base complexes, most are binuclear and there exist very few reports of high nuclearity 3d–4f salen based systems.<sup>2,5b,6</sup> Interestingly, **1** and **2** have a similar hexanuclear structures in the solid state with four  $\text{Eu}^{3+}$  cations bridged by eight  $\text{OAc}^-$  groups and clamped between two ML ( $\text{M} = \text{Ni}$  and  $\text{Cu}$ ) units. Intramolecular  $\pi$ – $\pi$  stacking interactions between phenylene units of  $\text{H}_2\text{L}$  are absent in the structures of **1** and **2**.

## Experimental section

### General considerations

All reactions were performed under dry oxygen-free dinitrogen atmospheres using standard Schlenk techniques. Metal salts and other solvents were purchased from Aldrich and used directly without further purification. The Schiff-base ligand  $\text{H}_2\text{L}$  was prepared according to well-established procedures.<sup>7</sup> Physical measurements: NMR: VARIAN UNITY-plus. 600 spectrometer ( $^1\text{H}$ , 600 MHz) at 298 K; Mass spec: HRESI, Finnigan MAT TSQ 700; IR: Nicolet IR 200 FTIR spectrometer. Melting points were obtained in sealed glass capillaries under dinitrogen and are uncorrected. Absorption spectra were obtained on a BECKMAN DU 640 spectrophotometer, excitation and visible emission spectra on a QuantaMaster PTI fluorimeter.

### Synthesis of complexes **1** and **2**

**$[\text{Eu}_4\text{Ni}_2\text{L}_2(\text{OAc})_{12}(\text{EtOH})_2]$  (**1**).** A mixture of the Schiff-base ligand  $\text{H}_2\text{L}$  (0.178 g, 0.5 mmol) and  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (0.124 g, 0.5 mmol) in  $\text{CH}_3\text{CN}/\text{EtOH}$  (1 : 3, 20 ml) was stirred and heated under reflux for 10 minutes. The reaction mixture was allowed to cool briefly,  $\text{Eu}(\text{OAc})_3 \cdot 4\text{H}_2\text{O}$  (0.165 g, 0.5 mmol) was added and the mixture was again heated under reflux (15 minutes).

It was allowed to cool and was then filtered. Diethyl ether was allowed to diffuse slowly into the filtrate at room temperature and blue crystals were obtained after two weeks. The crystals were filtered off and washed with  $\text{EtOH}$  (5 ml). Yield (based on  $\text{Eu}(\text{OAc})_3 \cdot 4\text{H}_2\text{O}$ ): 0.083 g (30%). m.p. > 290 °C (dec.). ESI-MS ( $\text{MeOH}$ )  $m/z$ : 1550 ( $[\text{NiEu}_3\text{L}(\text{OAc})_8(\text{EtOH})_4]^+$ ).  $^1\text{H}$  NMR (600 MHz,  $\text{CD}_3\text{OD}$ ):  $\delta$  (ppm) 91.990 (1H,  $\text{EtOH}$ ), 40.157 (2H), 16.249 (6H), 10.044 (4H), 3.599 (2H), 3.480 (3H), 1.166 (10H), –1.511 (18H). IR ( $\text{CH}_3\text{OH}$ ,  $\text{cm}^{-1}$ ): 3420 (m), 2951 (m), 1621 (s), 1553 (m), 1540 (m), 1451 (s), 1420 (s), 1340 (s), 1222 (m), 1075 (m), 856 (m), 730 (s).

**$[\text{Eu}_4\text{Cu}_2\text{L}_2(\text{OAc})_{12}] \cdot 2\text{H}_2\text{O}$  (**2**).** The procedure was the same as that for **1** using  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  (0.100 g, 0.5 mmol). Green blue single crystals of **2** were formed after two weeks. Yield (base on  $\text{Eu}(\text{OAc})_3 \cdot 4\text{H}_2\text{O}$ ): 0.135 g (48%). m.p. > 275 °C (dec.). ESI-MS ( $\text{MeOH}$ )  $m/z$ : 694 ( $[\text{CuEuL}(\text{OAc})_2]^+$ ).  $^1\text{H}$  NMR (600 MHz,  $\text{CD}_3\text{OD}$ ):  $\delta$  (ppm) 40.164 (2H), 18.487 (6H), 10.189 (2H), 8.809 (2H), 0.088 (6H), –2.340 (22H). IR ( $\text{CH}_3\text{OH}$ ,  $\text{cm}^{-1}$ ): 3379 (m), 1630 (s), 1557 (s), 1460 (s), 1418 (m), 1223 (s), 1156 (m), 1078 (m), 1001 (m), 855 (m), 732 (s).

### X-ray crystallography

Data were collected on a Rigaku MiniFlex II CCD diffractometer with graphite monochromated  $\text{Mo-K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 223 K. The data set was corrected for absorption based on multiple scans and reduced using standard methods. The structures were solved by direct methods and refined anisotropically using full-matrix least-squares methods with the SHELX 97 program package.<sup>8</sup> Coordinates of the non-hydrogen atoms were refined anisotropically, while hydrogen atoms were included in the calculation isotropically but not refined. Neutral atom scattering factors were taken from Cromer and Waber.<sup>9</sup>

## Results and discussion

Reactions of the Schiff-base ligand  $\text{H}_2\text{L}$  with  $\text{M}(\text{OAc})_2 \cdot n\text{H}_2\text{O}$  ( $\text{M} = \text{Ni}$  and  $\text{Cu}$ ) and  $\text{Eu}(\text{OAc})_3 \cdot 4\text{H}_2\text{O}$  in refluxing  $\text{MeCN}/\text{EtOH}$  (1 : 3) produced dark blue solutions from which the hexanuclear Ni–Eu and Cu–Eu complexes **1** and **2** were isolated as blue crystalline solids in 30 and 48% yields, respectively. The solid state structures of **1** and **2** were determined by single crystal X-ray crystallographic studies. Crystallographic data for both complexes are presented in Table 1 and selected bond lengths and angles are given in Tables 2 and 3.

A view of the crystal structure of **1** is shown in Fig. 1, and reveals a hexanuclear centrosymmetric core containing two equivalent  $\text{NiEu}_2\text{L}$  moieties linked by two tridentate  $\text{OAc}^-$  anions. In the  $\text{NiEu}_2\text{L}$  moiety,  $\text{Ni}(\text{I})$  is located in the inner  $\text{N}_2\text{O}_2$  cavity of the Schiff base ligand and has a bi-pyramidal geometry with two oxygen atoms from two bridged  $\text{OAc}^-$  anions occupying the axial positions.  $\text{Eu}(\text{I})$  is bound to the  $\text{O}_2\text{O}_2$  cavity of the Schiff-base ligand and surrounded by nine oxygen atoms from one L group and five  $\text{OAc}^-$  anions.  $\text{Ni}(\text{I})$  and  $\text{Eu}(\text{I})$  are bridged by two bidentate  $\text{OAc}^-$  anions in addition to the phenolic oxygen atoms of the Schiff base ligand. The  $\text{Ni}(\text{I})$ – $\text{Eu}(\text{I})$  separation is 3.346 Å.  $\text{Eu}(\text{2})$  and  $\text{Eu}(\text{1})$  are linked by three  $\text{OAc}^-$  anions with a separation of 4.113 Å.  $\text{Eu}(\text{2})$  is 9 coordinate being

**Table 1** Crystal data and structure refinement for complexes **1** and **2**

	<b>1</b>	<b>2</b>
Formula	C <sub>68</sub> H <sub>92</sub> N <sub>4</sub> O <sub>34</sub> Ni <sub>2</sub> Eu <sub>4</sub>	C <sub>64</sub> H <sub>88</sub> N <sub>4</sub> O <sub>36</sub> Cu <sub>2</sub> Eu <sub>4</sub>
Fw	2234.72	2224.24
Cryst syst.	Monoclinic	Triclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 1̄
<i>a</i> (Å)	12.803(3)	10.765(2)
<i>b</i> (Å)	16.488(3)	12.646(3)
<i>c</i> (Å)	19.716(4)	19.068(4)
$\alpha$ (°)	90	95.39(2)
$\beta$ (°)	108.40(3)	104.23(3)
$\gamma$ (°)	90	112.35(3)
<i>V</i> (Å <sup>3</sup> )	3949.3(14)	2275.9(10)
<i>Z</i>	2	1
<i>D</i> <sub>calc</sub> (g cm <sup>−3</sup> )	1.879	1.617
Temp (K)	153(1)	153(1)
<i>F</i> (000)	2216	1090
$\mu$ (mm <sup>−1</sup> )	3.685	3.251
$\theta$ rang (°)	1.65–25.00	1.13–25.00
Refins meads	10 575	19 984
Refins used	6850	7993
Params	505	516
<i>R</i> <sup>a</sup> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	<i>R</i> <sub>1</sub> = 0.0367 w <i>R</i> <sub>2</sub> = 0.1101	<i>R</i> <sub>1</sub> = 0.0570 w <i>R</i> <sub>2</sub> = 0.1662
<i>R</i> <sup>a</sup> (all data)	<i>R</i> <sub>1</sub> = 0.0446 w <i>R</i> <sub>2</sub> = 0.1358	<i>R</i> <sub>1</sub> = 0.0829 w <i>R</i> <sub>2</sub> = 0.2038
<i>S</i>	1.221	1.171

$$^a R_1 = \sum |F_o| - |F_c| / \sum |F_o|, wR_2 = [\sum w[(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2]^{1/2}, w = 1/[\sigma^2(F_o^2) + (0.075P)^2], \text{ where } P = [\max(F_o^2, 0) + 2F_c^2]/3.$$

**Table 2** Selected bond lengths (Å) and angles (°) for **1**

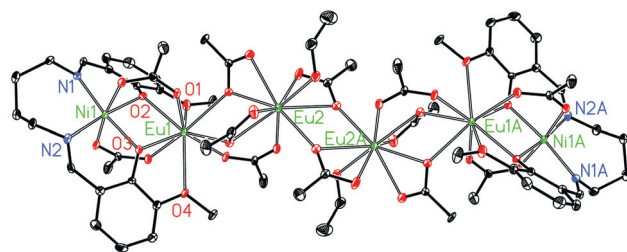
Eu(1)–O(3)	2.336(5)
Eu(1)–O(2)	2.337(4)
Eu(1)–O(9)	2.359(5)
Eu(1)–O(8)	2.390(4)
Eu(1)–O(6)	2.397(4)
Eu(1)–O(13)	2.495(4)
Eu(1)–O(11)	2.542(5)
Eu(1)–O(4)	2.643(5)
Eu(1)–O(1)	2.667(5)
Ni(1)–O(3)	2.063(5)
Ni(1)–O(7)	2.080(5)
Ni(1)–N(1)	2.087(6)
Ni(1)–O(2)	2.092(5)
Ni(1)–O(5)	2.099(5)
Ni(1)–N(2)	2.126(6)
O(3)–Eu(1)–O(2)	75.80(16)
O(3)–Eu(1)–O(4)	62.73(15)
O(2)–Eu(1)–O(4)	133.64(15)
O(3)–Eu(1)–O(1)	131.67(16)
O(2)–Eu(1)–O(1)	63.03(16)
O(4)–Eu(1)–O(1)	134.77(17)
O(3)–Ni(1)–N(1)	171.9(2)
O(3)–Ni(1)–O(2)	87.40(17)
N(1)–Ni(1)–O(2)	85.2(2)
O(3)–Ni(1)–N(2)	87.5(2)
O(7)–Ni(1)–N(2)	94.33(19)
N(1)–Ni(1)–N(2)	100.0(2)
O(2)–Ni(1)–N(2)	174.6(2)

bound by five OAc<sup>−</sup> anions and one EtOH molecule. The distance between the two central Eu(2) ions is 4.231 Å.

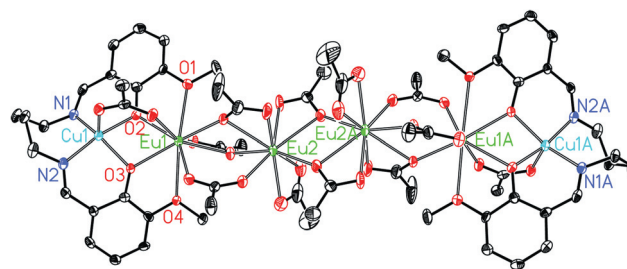
A view of the crystal structure of **2** is shown in Fig. 2. Complex **2** has a similar hexanuclear structure to **1**, thus there is a centrosymmetric core with two equivalent CuEu<sub>2</sub>L moieties

**Table 3** Selected bond lengths (Å) and angles (°) for **2**

Eu(1)–O(6)	2.309(7)
Eu(1)–O(3)	2.372(6)
Eu(1)–O(9)	2.396(7)
Eu(1)–O(11)	2.414(7)
Eu(1)–O(2)	2.441(6)
Eu(1)–O(7)	2.495(8)
Eu(1)–O(8)	2.525(7)
Eu(1)–O(1)	2.663(8)
Eu(1)–O(4)	2.794(7)
Cu(1)–O(2)	1.955(7)
Cu(1)–N(1)	2.003(8)
Cu(1)–O(3)	2.006(7)
Cu(1)–N(2)	2.012(9)
Cu(1)–O(5)	2.156(7)
O(3)–Eu(1)–O(2)	63.9(2)
O(3)–Eu(1)–O(1)	125.3(2)
O(2)–Eu(1)–O(1)	61.7(2)
O(3)–Eu(1)–O(4)	59.2(2)
O(2)–Eu(1)–O(4)	104.7(2)
O(1)–Eu(1)–O(4)	141.1(3)
O(2)–Cu(1)–N(1)	91.1(3)
O(2)–Cu(1)–O(3)	80.0(3)
N(1)–Cu(1)–O(3)	146.4(3)
O(2)–Cu(1)–N(2)	170.5(3)
N(1)–Cu(1)–N(2)	95.9(3)
O(3)–Cu(1)–N(2)	90.6(3)



**Fig. 1** A view of the crystal structure of **1**. H atoms have been omitted for clarity and thermal ellipsoids drawn at the 30% probability level. Symmetry operator (−*x*, −*y*, −*z*) generates equivalent atoms marked with “A”.



**Fig. 2** A view of the crystal structure of **2**. H atoms have been omitted for clarity and thermal ellipsoids drawn at the 30% probability level. Symmetry operator (−*x*, −*y*, −*z*) generates equivalent atoms marked with “A”.

that are bridged by two tridentate OAc<sup>−</sup> anions. The distance between the two equal Eu(2) ions is 4.144 Å. In the CuEu<sub>2</sub>L moiety, Cu(1) and Eu(1) are located in the inner N<sub>2</sub>O<sub>2</sub> and O<sub>2</sub>O<sub>2</sub> cavities of the Schiff-base ligand, respectively, with a separation of 3.467 Å. The Cu<sup>2+</sup> ion has a square based pyramidal

geometry *via* the coordination of an oxygen atom of OAc<sup>−</sup> anion in the axial position. Eu(1) has a nine-coordinate environment similar to that found in **1**. Eu(2) and Eu(1) are also linked by three OAc<sup>−</sup> anions with a separation of 4.087 Å. However, unlike **1** there is no EtOH molecule coordinated to Eu(2). Eu(2) is 9 coordinate being bound by six OAc<sup>−</sup> anions. In **1** and **2**, the average distances for the Ni–N (2.107 Å), Ni–O (phenolic) (2.078 Å), Cu–N (2.009 Å), Cu–O (phenolic) (1.980 Å), Eu–O (phenolic) (2.337 Å **1**, 2.408 Å **2**) and Eu–O(methoxy) (2.655 Å **1**, 2.732 Å **2**) bonds are comparable to those found in the literature.<sup>5,6</sup>

<sup>1</sup>H NMR spectrum of **1** in CD<sub>3</sub>OD at room temperature revealed the presence of 7 broadened peaks ranging from −2 to +41 ppm, corresponding to the 45 C–H protons from one Schiff base ligand, six coordinated OAc<sup>−</sup> groups and one coordinated EtOH molecule (Fig. S1, ESI†). A very broad O–H proton peak assigned to the coordinated EtOH is observed at +92 ppm. The <sup>1</sup>H NMR spectrum of **2** in CD<sub>3</sub>OD at room temperature shows the presence of 6 broadened peaks ranging from −3 to +41 ppm. These peaks correspond to the 40 C–H protons from one Schiff base ligand and six coordinated OAc<sup>−</sup> groups. The broad and unresolved nature of the signals caused by the paramagnetic 3d metal ions and the 4f lanthanide ions precluded further study by COSY 2-D analysis. The data is consistent with multinuclear structures for **1** and **2** persisting in solution.

### Luminescence studies

There is considerable interest in luminescent lanthanide complexes since lanthanide ions exhibit long-lived lifetimes and line-like emission bands at characteristic wavelengths. The photophysical properties of lanthanide ions depend markedly on the environment surrounding the metal center. For example, solvents containing O–H (*i.e.* H<sub>2</sub>O and CH<sub>3</sub>OH) can efficiently quench the luminescence of lanthanide ions. However, if the O–H is replaced by O–D, this process becomes much less efficient.<sup>10</sup> Since complexes **1** and **2** are soluble in methanol the photophysical properties were studied in both CH<sub>3</sub>OH and CD<sub>3</sub>OD.

The absorption spectra of the free ligand H<sub>2</sub>L, and complexes **1** and **2** in MeOH are shown in Fig. 3. The free ligand H<sub>2</sub>L exhibits absorption bands at 219, 240, 259, 291 and 415 nm, which are strongly perturbed upon co-ordination to Ln<sup>3+</sup> in complexes **1** and **2**. Complexes **1** and **2** exhibit similar solution absorption spectra. The excitation and emission spectra of the free ligand H<sub>2</sub>L and complex **1** are shown in Fig. 4. Excitation of the absorption band at 275 nm of the free ligand H<sub>2</sub>L produces two broad emission bands at λ<sub>max</sub> = 319 and 496 nm. The excitation spectrum of the free ligand H<sub>2</sub>L, monitoring the intensity of the emission at 496 nm, displays two peaks centered at 275 and 350 nm. For complexes **1** and **2**, the typical narrow emission bands of the Eu<sup>3+</sup> ion (<sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>*j*</sub> transitions, *j* = 0, 1, 2, 3 and 4) can be detected upon excitation of the ligand-centered absorption bands (λ<sub>ex</sub> = 308 and 281 nm for **1** and **2**, respectively) in CD<sub>3</sub>OD at room temperature (Fig. 4). However, the emission intensities are reduced sharply in CH<sub>3</sub>OH, indicating that the photophysical properties are significantly affected by solvent O–H bonds in the solvent molecules. The overall quantum yield

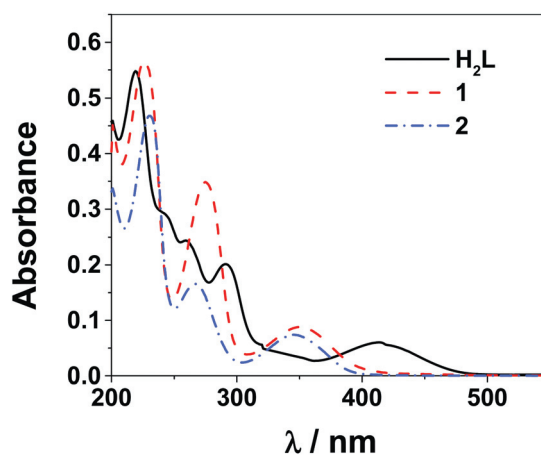


Fig. 3 Absorption spectra of the free H<sub>2</sub>L and complexes **1** and **2** in CH<sub>3</sub>OH.

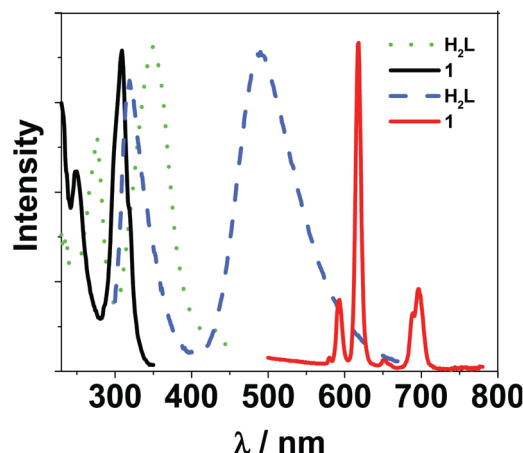


Fig. 4 Excitation and emission spectra of the free ligand H<sub>2</sub>L (···; ---) in CH<sub>3</sub>OH and **1** (—) in CD<sub>3</sub>OD at room temperature.

(Φ<sub>em</sub>) of **1** in CD<sub>3</sub>OD was determined as 0.0011 relative to [Ru(bipy)<sub>3</sub>]Cl<sub>2</sub> in water (bipy = 2,2'-bipyridine; Φ<sub>em</sub> = 0.028),<sup>11</sup> which is less than that of the polymeric complex [Eu<sub>2</sub>(H<sub>2</sub>L)-(OAc)<sub>6</sub>]<sub>n</sub> that does not bear 3d metal ions (Φ<sub>em</sub> = 0.015).<sup>5i</sup> The luminescence of **2** in CD<sub>3</sub>OD is also weak with a quantum yield less than 10<sup>−4</sup>. For both **1** and **2**, the weak luminescence of Eu<sup>3+</sup> ions maybe due to lanthanide to transition metal (4f → 3d) energy transfer which can efficiently quench lanthanide ions.<sup>12</sup> Studies of other d-block metals (*i.e.* d<sup>10</sup> monovalent metal ions<sup>13</sup>) in the synthesis of d–f complexes, which may result in the transition metal to lanthanide (d → 4f) energy transfer, are in progress.

### Conclusions

Two hexanuclear Ni–Eu and Cu–Eu complexes **1** and **2** with the flexible Schiff-base ligand H<sub>2</sub>L have been prepared and structurally characterized. In complexes **1** and **2**, four Eu<sup>3+</sup> anions bridged by eight OAc<sup>−</sup> groups are clamped between two ML (M = Ni and Cu) units. The overall structures of **1** and **2** comprise two crystallographically equivalent MEu<sub>2</sub>L units related by



a center of symmetry and linked by two OAc<sup>−</sup> groups. Both **1** and **2** show visible emissions of Eu<sup>3+</sup> ions in methanol. However, the overall quantum yields of **1** and **2** are much less than that of [Eu<sub>2</sub>(H<sub>2</sub>L)(OAc)<sub>6</sub>]<sub>n</sub>, indicating that the energy transfer from the Eu<sup>3+</sup> ions to the transition metals (Ni<sup>2+</sup> and Cu<sup>2+</sup>) may happen in **1** and **2**.

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